

AGRICULTURAL HERBICIDE TRANSPORT IN A FIRST-ORDER INTERMITTENT STREAM, NEBRASKA, USA

J. R. Vogel, J. I. Linard

ABSTRACT. *The behavior of herbicides in surface waters is a function of many variables, including scale of the watershed, physical and chemical properties of the herbicide, physical and chemical properties of the soil, rainfall intensity, and time of year. In this study, the transport of 6 herbicides and 12 herbicide degradates was examined during the 2004 growing season in an intermediate-scale agricultural watershed (146 ha) that is drained by a first-order intermittent stream, and the mass load for each herbicide in the stream was estimated. The herbicide load during the first week of storm events after application ranged from 17% of annual load for trifluralin to 84% of annual load for acetochlor. The maximum weekly herbicide load in the stream was generally within the first 3 weeks after application for those compounds that were applied within the watershed during 2004, and later for herbicides not applied within the watershed during 2004 but still detected in the stream. The apparent dominant mode of herbicide transport in the stream--determined by analysis amongst herbicide and conservative ion concentrations at different points in the hydrograph and in base flow samples--was either overland runoff or shallow subsurface flow, depending on the elapsed time after application and type of herbicide. The load as a percentage of use (LAPU) for the parent compounds in this study was similar to literature values for those compounds applied by the farmer within the watershed, but smaller for those herbicides that had rainfall as their only source within the watershed.*

Keywords. *Herbicides, Contaminant transport, Degradates, Mass load.*

Herbicides may be transported from their intended area of application to other areas of the environment. The pathways for this transport from the area of application can include movement through the soil, overland flow of water to streams or other surface water bodies, or atmospheric transport. Much of the research on transport of agricultural chemicals in surface water has been completed either on small-scale research plots (<50 ha) or large-scale perennial river basins (>1000 ha). Capel and Larson (2001) indicated the absence of studies on “intermediate-scale” watersheds (50-1000 ha) regarding atrazine in runoff and streams. This intermediate scale generally represents the headwater catchment of first-order streams.

Further literature review by the authors identified three additional studies that investigate atrazine transport in nine watersheds at the intermediate scale (Wu et al., 1983; Hyer et al., 2001; Leu, et al., 2005) that were not included in Capel and Larson (2001).

The chemical and physical properties of each herbicide can affect its persistence in the hydrologic system. Sorption (often quantified by K_{oc}), volatilization (often modeled by vapor pressure), and degradation [often quantified by half life

($t_{1/2}$) in soil or water] of these compounds may all affect their persistence in the aqueous phase (Barbash, 2003). Three studies of atrazine runoff at the intermediate scale have indicated that most of the transport of atrazine takes place during precipitation events occurring within one month of the herbicide’s application within the watershed (Wu et al., 1983; Hyer et al., 2001; Leu et al., 2005).

Many studies have shown that during a storm, the highest herbicide concentrations occur during the rising limb of the stream hydrograph, especially during the first storm after application (Anderson et al., 1997; Williams, 1998; Hyer et al., 2001; McHale and Phillips, 2001; Williams and Clark, 2001; Kronvang et al., 2003). A few exceptions to this include Kronvang et al. (2003), where researchers detected peak concentrations of isoproturon during the falling limb of a storm hydrograph in a tile-drained watershed. Kronvang et al. (2003) attributed the peak concentration lagging the peak discharge to movement of the pesticide through the soil-to-tile drains and then to the stream. During the same storms, however, the highest concentrations for diuron and terbutylazin occurring during the rising limb of the hydrograph. Williams and Clark (2001) also detected the highest concentration of diazinon during the recession of a hydrograph for an August storm in Deer Creek in Pennsylvania, although the highest concentration of prometon was detected during the rising limb of the storm hydrograph. A dilution effect was noted by Anderson et al. (1997) for atrazine concentrations at the peak discharge in a stream in Oregon, while the metolachlor concentrations decreased throughout the duration of the storm hydrograph. This was attributed to the fact that the surface runoff that contributed to the rising limb of the hydrograph was depleted of metolachlor, but enriched in atrazine, compared to concentrations already in the stream. Roman-Mas et al. (1995) showed that the concentration of aldicarb in a

Submitted for review in January 2010 as manuscript number SW 8406; approved for publication by the Soil & Water Division of ASABE in August 2010.

The authors are **Jason R. Vogel, ASABE Member Engineer**, Assistant Professor, Biosystems and Agricultural Engineering Department, Oklahoma State University, Stillwater, Oklahoma and **Joshua I. Linard**, Hydrologist, U.S. Geological Survey Colorado Water Science Center, Grand Junction, Colorado. **Corresponding author:** Jason R. Vogel, Biosystems and Agricultural Engineering, Oklahoma State University, 218 Ag Hall, Stillwater, OK 74078; phone: 405-744-7532, fax: 405-744-6059, e-mail: jason.vogel@okstate.edu.

first-order stream in west Tennessee increased linearly with time and inversely in proportion to the rainfall-runoff ratio to the point of maximum concentration. The duration of this initial pattern was similar to the basin response (lag) time.

The load as a percentage of use (LAPU) has been previously defined by Capel and Larson (2001) as a method to normalize the annual load of a pesticide for comparison between watersheds. Using the LAPU, Capel and Larson (2001) suggest that the average runoff behavior of atrazine in a wide variety of watersheds was consistent. Capel et al. (2001) further applied the LAPU to 39 pesticides including atrazine and separated the pesticides into three general groups: (1) pesticides that are seldom seen in surface water; (2) pesticides that show little, if any, loss within the stream network; and (3) pesticides that show in-stream losses. The pesticides that show in-stream losses were defined as those that had mean LAPU value in larger watersheds (between 100 and 100,000 ha) that were at least two magnitudes smaller than the mean LAPU value in smaller watersheds (<60 ha). Herbicides which showed little, if any, in-stream losses included alachlor, atrazine, and metolachlor. Trifluralin was shown to exhibit in-stream losses. The herbicides acetochlor and glyphosate were not included in the analysis by Capel et al. (2001).

The herbicides atrazine, acetochlor, alachlor, metolachlor, glyphosate, and trifluralin were all among the 10 most used herbicides in the agricultural sector in the

United States in 2001 (Kiely et al., 2004). The objective of this study was to investigate the fate and transport of these 6 herbicides and 12 of their degradates in an intermediate-scale agricultural watershed (146 ha) that is drained by a first-order intermittent stream in eastern Nebraska. Water samples were collected and analyzed for these herbicides for the 2004 growing season. Additionally, the watershed was modeled using Soil and Water Assessment Tool (SWAT, version 2000; Neitsch et al., 2002), and the annual load for each herbicide was estimated. Comparisons of herbicide loads during base flow and storm events were made. The LAPU was compared for the different pesticides and compared to values found in the literature when available. Finally, pesticide concentrations during different parts of individual storms were calculated and compared. Using this information, the predominant transport pathway during the period of highest loading was identified for each of the herbicides and herbicide degradates investigated in this study.

The six parent herbicides analyzed during this study are summarized in table 1. All of these herbicides are applied to corn (not the glyphosate tolerant variety) and/or soybeans, which were the two prevalent crops in the study area. Atrazine, a triazine herbicide, has been shown to be relatively persistent, especially in dry or cold conditions (Howard, 1989), and has primary degradation pathways of chemical hydrolysis and degradation by soil microorganisms.

Table 1. Major crops, primary application method, chemical properties, and degradates analyzed for the six parent compounds included in this study.^[a]

Pesticide	Major Crops Applied to in the Area	Primary Application Method	Water Solubility at 25°C (mg/L)	K _{oc} ^[b] (mL/g)	t _{1/2} in Soil ^[c] (days)	Vapor Pressure at 25°C (Pa)	Degradates Analyzed ^[d]
Atrazine	Corn, sorghum	May be applied as a surface application before or after planting (most common), or incorporated into the soil after planting	33	100	60	3.85 × 10 ⁻⁵	Deethylatrazine
Acetochlor	Corn, soybeans, sorghum	May be applied as a surface application before or after planting (most common), or incorporated into the soil after planting	223	315	16	4.53 × 10 ⁻⁶	Acetochlor ESA, Acetochlor OXA, Acetochlor SAA, Acetochlor/ Metolachlor ESA – 2nd amide
Alachlor	Corn, soybeans, sorghum	May be applied as a surface application before or after planting (most common), or incorporated into the soil after planting	240	170	15	1.87 × 10 ⁻³	Alachlor ESA, Alachlor OXA, Alachlor SAA, Alachlor ESA – 2nd amide
Metolachlor	Corn, sorghum	May be applied as a surface application before or after planting (most common), or incorporated into the soil after planting	530	200	90	4.19 × 10 ⁻³	Metolachlor ESA, Metolachlor OXA
Glyphosate	Corn, soybeans	Surface applied after planting and during the growing season as needed	10,100	24,000 ^[e]	2	<1 × 10 ⁻⁵	AMPA
Trifluralin	Soybeans, winter wheat, alfalfa	Generally incorporated into the soil after planting, but may also be surface applied	0.3	8,000	60	1.47 × 10 ⁻²	None

[a] All pesticide properties are from Capel et al. (2008) except as noted.

[b] K_{oc}: soil organic carbon-water partitioning coefficient.

[c] t_{1/2}: half life.

[d] ESA: ethane sulfonic acid; OXA:oxanilic acid; SAA: sulfynil acetic acid; 2nd: second; AMPA: aminomethylphosphonic acid.

[e] Wauchope et al., 1992.

Acetochlor, alachlor and metolachlor are chloracetamide herbicides with persistence of these herbicides in soil affected by many factors, including the organic content of the soil, resident microbial population, soil temperature, nitrogen and phosphorus bioavailability, water content, and soil texture. Alachlor has a low persistence in soil, while acetochlor and metolachlor are moderately persistent in the soil. Glyphosate, a broad-spectrum, non-selective systemic herbicide, is moderately persistent in soil and is strongly adsorbed to most soils, even those with lower organic and clay content (Wauchope et al., 1992). Microbes are primarily responsible for the breakdown of glyphosate. Trifluralin, a selective, pre-emergence dinitroaniline herbicide, is generally incorporated into the soil by tilling within 24 h of application, is of moderate to high persistence in the soil, depending on conditions, is subject to degradation by soil microorganisms, and is nearly insoluble in water.

Further information on this site is available in Fredrick et al. (2006).

The drainage area at the gage was approximately 146 ha, and its land use is approximately 97% cropland (corn, soybeans, and alfalfa). The most predominant soil association within the watershed is Nora-Crofton-Moody (Bartlett and Koepke, 1975). The watershed is characterized by rolling hills of loess-mantled glacial till. Regional groundwater is generally found at depths greater than 100 m below ground surface. Elevations in the watershed range from approximately 500 m in the upper part of the watershed to approximately 450 m, measured from North American Vertical Datum of 1988. The climate is typical of a humid continental region that is characterized by hot summers and cold winters. At the National Weather Service station in nearby Columbus, Nebraska (Station 251825), which is located approximately 30 km southwest of the study site, mean annual precipitation was 723 mm for the period between 1948 and 2003 (U.S. Department of Commerce, 2005). Total annual precipitation at Columbus was 649 and 721 mm in 2003 and 2004, respectively. Precipitation is typically greatest in May and June when convective thunderstorms produce intense, short-duration periods of rainfall (Huntzinger and Ellis, 1993). Center pivots irrigated 35% of the watershed, with a total of approximately 950,000 L applied between July and August, 2004. In general, the intermittent stream at the site started to flow after the first large rain in the spring, and continued flowing until August or September. The base flow in the stream was fed by springs created by shallow subsurface flow from precipitation and irrigation at the site. The irrigation in the watershed may have also contributed to an increase in overland runoff from late-summer precipitation and to the flow from the springs during the late summer by increasing the antecedent moisture content of the soil. Based upon farmer interviews, all the cropped areas in the watershed were in no-tillage practices in 2004, and different sections of the watershed had been

METHODS AND MATERIALS

SITE DESCRIPTION

This study was conducted in a small agricultural watershed in Colfax County in northeast Nebraska drained by an unnamed tributary to the South Fork of Dry Creek. For purposes of this study, a seasonal U.S. Geological Survey (USGS) stream gage (USGS Station 06799750) was established on this tributary. This is a first-order intermittent stream located approximately 13 km northwest of Schuyler, Nebraska (fig. 1). The period of record for this site was intermittent from June 2003 through December 2004. Stage was measured using a triple-orifice bubbler, with discharge calculated either using the Cone Equation for discharge over the 90° V-notch weir (Bureau of Reclamation, 2001, eq. 1) for flows under 0.0011 m³/s, or using a conversion table created with the Culvert Analysis Program (Fulford, 1998) for the 1.98-m corrugated culvert for flows greater than 0.0011 m³/s.

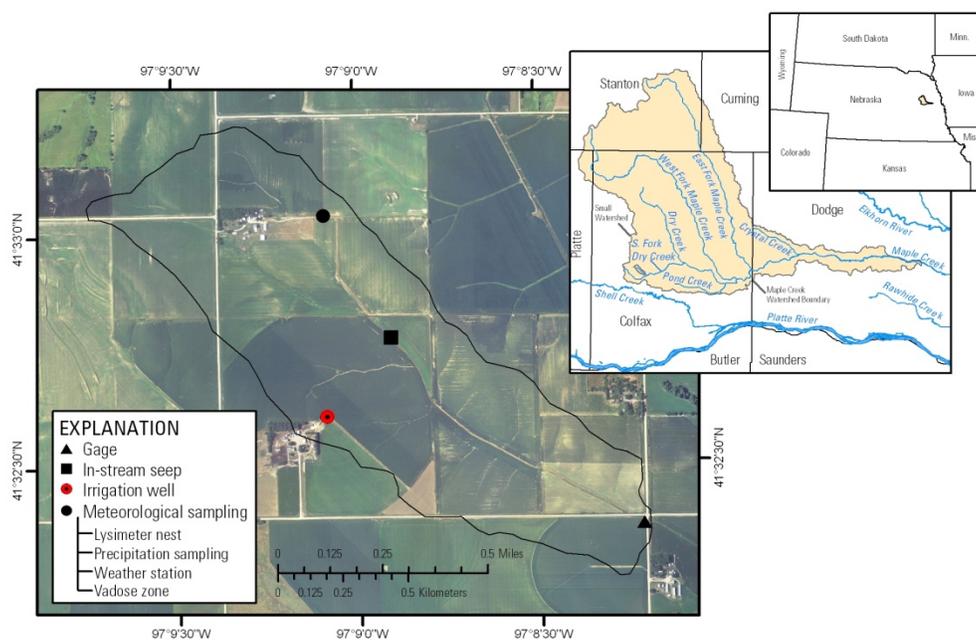


Figure 1. Location of sampling sites located in the watershed of the unnamed tributary to the South Fork of Dry Creek in Colfax County, Nebraska.

operated with no-till practices for the previous zero to more than 10 years. Previous to the no-till practices, the cropped areas had been operated as conventional tillage which included disking, chisel plowing, and moldboard plowing. More than half of the agricultural area in the watershed was in its first year of no-till in 2004, after one year of minimum tillage as a transition from conventional tillage. There were no tile drains in this watershed. Approximately 11 kg of atrazine, 28 kg of acetochlor, and 55 kg of trifluralin were applied during planting within the watershed of the South Fork of Dry Creek tributary during the first week of May 2004, and 52 kg of glyphosate were applied on 5 July 2004. The application of these compounds was spread among 14 individual cropped areas within the watershed, with no particular upstream to downstream pattern in their distribution. Other herbicides with more than 1,000 kg of applications within the surrounding Maple Creek watershed during 2004 include pendimethalin, metolachlor, alachlor, and dimethenamid (Fredrick et al., 2006). The cropped fields in this watershed have been cultivated by the same families since agricultural activity began, and the current residents indicated that, to their knowledge, alachlor and metolachlor had never been applied to the watershed.

SAMPLING AND LABORATORY ANALYSIS

In 2004, surface-water samples were collected adjacent to the gage through Teflon[®] tubing by an automatic sampler during selected storm events (10 May, 13 May, 22 May, 7 July, 22 July, 25 August, and 23 September) and downstream of the weir as grab samples during base flow conditions (12 May, 22 May, 2 June, 16 June, 29 June, and 31 August). A grab sample was also collected downstream of the weir during a storm on 8 May 2004, at the hydrograph peak because of an equipment malfunction. The samples were collected in Teflon or glass bottles, and using Teflon[®] tubing, to minimize contamination. Water samples for herbicides were collected and processed by filtering through glass-fiber 0.7- μ m filters. Rain samples were collected through Teflon-lined funnels into refrigerated containers to compose weekly composites, and then processed in a manner similar to water samples. Vadose zone pore-water samples were collected in ceramic porous-cup suction lysimeters located at 1.5, 2.4, 4.0, and 7.6 m below land surface on a hillslope under an agricultural field. The samples were collected after applying suction for 12 to 24 h on the day following a storm event. Grab samples also were collected from the irrigation pipe near the well and from seepage water near the headwaters of the stream for water quality analysis. Locations of the sampling sites are shown on figure 1.

For quality assurance/quality control (QA/QC) purposes, two field blank samples and one concurrent replicate sample (on 29 June 2004, during base flow conditions) were collected during the study. Neither of the blank samples had detections of any of the herbicides or herbicide degradates discussed in this article. The largest difference between the concentration in the environmental and concurrent replicate sample was 0.09 μ g/L (64%) for acetochlor oxanilic acid (OXA). Water volume limitations in autosampler samples collected during storm events limited the number of replicate samples that could be collected.

Herbicide analysis for atrazine, deethylatrazine, trifluralin, acetochlor, alachlor, and metolachlor was by gas chromatography/mass spectrometry (GC/MS) according to

the method of Zaugg et al. (1995). Analysis of acetanilide degradation products was completed by liquid chromatography/mass spectrometry (LC/MS) using the method of Lee and Strahan (2003). All samples were analyzed for glyphosate and aminomethyl phosphonic acid (AMPA) using a precolumn derivatization with 9-fluorenylmethylchloroformate followed by an automated online solid-phase extraction and direct injection into a LC/MS (Lee et al., 2002). Chloride and sulfate ions were also analyzed in these samples by ion chromatography (IC) (Pfaff, 1993). Further details on sampling, analytical, and QA/QC methods are available in Capel et al. (2008).

TIME-OF-TRAVEL STUDY

To determine the residence time of water within the stream during base flow conditions, two time-of-travel studies were completed on successive days in June 2004. The time-of-travel studies used Rhodamine water tracing (WT) 20% dye to monitor the movement of water within the stream following the methods of Kilpatrick and Wilson (1989). Approximately 1 L and 3 L of dye solution were poured in the tributary of the South Fork of Dry Creek on 2 and 3 June, respectively. Samples were collected manually at the center of flow near the USGS gage located 1175 m downstream of the release point, and analyzed using a fluorimeter. Sampling intervals varied throughout the experiment, with the shortest intervals (2 min) during the time nearest the peak concentration in the stream at the sampling point. Time of travel was determined by calculating the time lapse from release of the dye to peak concentration at the sampling point.

LOAD CALCULATIONS AND MODELING

The loads of herbicide in the South Fork of Dry Creek tributary were calculated by interpolation between times of streamflow and sampling events, and when necessary, using modeled results for discharge from SWAT. A SWAT model (version 2000, Neitsch et al., 2002) was developed to synthesize streamflow during periods when the stream gage on the South Fork of Dry Creek tributary was inoperable. SWAT has been widely used to model hydrologic and contaminant transport processes in agricultural areas (Gassman et al., 2007).

The preprocessing software, Better Assessment Science for Integrating point and Non-point Sources (BASINS) (USEPA, 2004), was used to create the default parameter files necessary for initial simulations. A 10-m resolution digital elevation model (DEM), was used to characterize terrain for land-use and soil map units (USGS, 2006). The spatial representation of land use was developed by digitizing each field from digital orthophoto quadrangles. The map-unit grid corresponding to the State Soil Geographic (STATSGO) database (Schwarz and Alexander, 1995) was used for soils information and had a 30-m resolution. Simulations were designed to run at a daily time-step from 1 October 2002, through 30 September 2004. Climatic data used in simulations were obtained from a weather station installed in the watershed. The model was manually calibrated by visually matching simulated hydrographs of streamflow to streamflow measured at the stream gage. Additionally, the annual evapotranspiration simulated by the model using the Penman-Monteith equation was compared to the mean annual value of 500 mm presented by Dugan and Zelt (2000).

RESULTS AND DISCUSSION

STREAMFLOW

The simulated streamflow corresponded to the intermittent nature of the South Fork of Dry Creek tributary (fig. 2). In the simulation, streamflow was sustained from 22 May 2004, through, at least, 30 September 2004. A maximum streamflow of 0.33 m³/s was simulated in 2004 while the mean streamflow for 2004 was 0.0039 m³/s. Simulation results indicated that on an annual basis about 11% of precipitation leaves the watershed as streamflow. Of the simulated streamflow amounts, 37% can be attributed to springs responding to rain events and irrigation (response time in days to weeks), 53% resulting from a quick response of the shallow subsurface to precipitation (response time in hours), and 10% from direct surface runoff.

A time-of-travel study was completed on 2 June and repeated on 3 June 2004, to determine residence time of water within the stream during base flow conditions. At the time of the study, flow in the stream was approximately 0.007 m³/s. The two tests showed similar results, with an average time of travel from the release point at the headwaters of the stream to the water-quality sampling point (1175 m) of approximately 6 h (fig. 3). Additionally, based upon this time of travel, average in-stream velocity in the reach was 3.3 m/min.

HERBICIDES

Flow-weighted stream-water samples were collected during storms and irregularly during base flow conditions. The water-quality results from these samples are summarized in table 2. When possible, storm samples were analyzed both as a whole-storm flow-weighted composite and subdivided into rise, peak, and fall samples. The parent herbicides that were applied within the watershed (glyphosate, acetochlor, atrazine, and trifluralin) were generally the ones that were detected at the highest concentrations in the stream. However, the parent compounds metolachlor and alachlor were detected at low concentrations in most stream samples, even though there was no reported use within the watershed.

Glyphosate was also detected before it was reported applied on 7 July within the watershed.

In general, the atrazine, acetochlor, and trifluralin concentrations showed decreasing trends in base flow after the date of application within the watershed (fig. 4). The lag time between the maximum acetochlor concentration in a storm-event flow-weighted composite sample, and the maximum acetochlor degradate concentration in a storm-event flow-weighted composite sample ranged from 0 days for acetochlor OXA to 14 days for acetochlor ESA. For atrazine and deethylatrazine, this lag time was two days. Including the storm when the maximum acetochlor and atrazine concentrations occurred, there were four storms during the 14-day period between 8 and 22 May.

Maximum concentrations in base flow stream samples for all four herbicides applied within the watershed in 2004, and for their degradates, occurred within 3 weeks of application (fig. 4; table 2). Alachlor and metolachlor, which had no reported applications in the watershed in 2004, also showed peak base flow concentrations in May. The peak

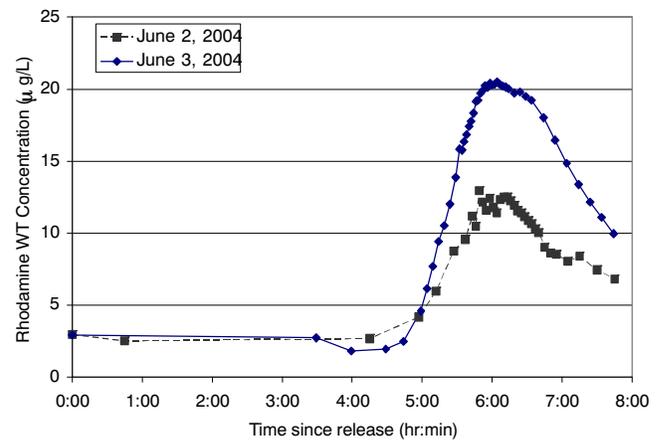


Figure 3. Time of travel for Rhodamine WT dye tracer in the tributary to South Fork of Dry Creek during base flow conditions.

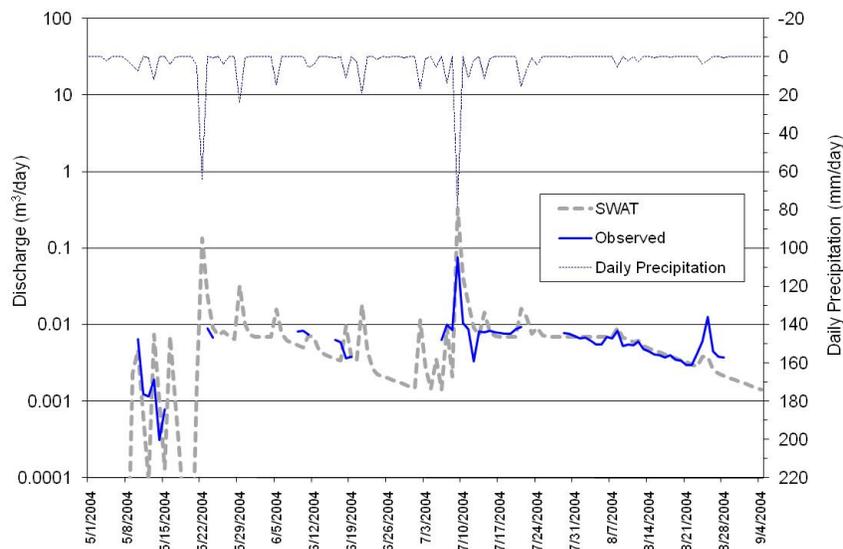


Figure 2. Rainfall and simulated and observed streamflow in the tributary to South Fork of Dry Creek from 1 May through 1 September 2004. Broken parts of the observed line is due to equipment failure.

Table 2. Summary of herbicide detections and concentrations in samples collected from the unnamed tributary to the South Fork of Dry Creek.^[a]

Herbicide Compound (LRL) ^[c]	Storm Event Samples ^[b]				Base Flow Samples				
	No. of Samples	No. of Detects	Max Conc. (µg/L)	Date of Max Conc.	No. of Samples	No. of Detects	Median Conc. (µg/L)	Max Conc. (µg/L)	Date of Max Conc.
Glyphosate (0.1)	16	14	9.7	7-Jul-04	5	3	0.2	1.0	29-Jun-04
AMPA (0.1)	16	14	5.4	7-Jul-04	5	4	0.7	1.2	29-Jun-04
Acetochlor (0.006)	17	17	215	8-May-04	6	5	0.12	3.03	22-May-04
Acetochlor ESA (0.02)	16	15	10.0	22-May-04	6	5	0.19	5.38	22-May-04
Acetochlor OXA (0.02)	16	15	15.0	8-May-04	6	5	0.15	13.0	22-May-04
Acetochlor SAA (0.02)	16	13	8.47	10-May-04	6	2	<0.02	5.44	22-May-04
Acetochlor/ Metolachlor ESA - 2nd amide (0.02)	16	13	0.47	13-May-04	6	4	0.03	0.53	22-May-04
Alachlor (0.005)	16	13	0.15	10-May-04	6	3	<0.04	0.05	22-May-04
Alachlor ESA (0.02)	16	13	0.17	13-May-04	6	4	0.03	0.09	22-May-04
Alachlor OXA (0.02)	16	14	0.19	13-May-04	6	3	<0.02	0.05	22-May-04
Alachlor SAA (0.02)	16	11	2.79	13-May-04	6	2	<0.02	1.29	22-May-04
Alachlor ESA - 2nd amide (0.02)	16	5	0.14	10-May-04	6	1	<0.02	0.02	31-Aug-04
Metolachlor (0.013)	16	15	0.73	7-Jul-04	6	4	0.01	0.10	22-May-04
Metolachlor ESA (0.02)	16	14	0.19	10-May-04	6	5	0.12	0.21	31-Aug-04
Metolachlor OXA (0.02)	16	14	0.17	22-May-04	6	5	0.03	0.06	22-May-04
Atrazine (0.007)	16	16	191	8-May-04	6	6	0.27	5.27	22-May-04
Deethyl-atrazine (0.006)	16	16	1.67	10-May-04	6	6	0.03	0.51	22-May-04
Trifluralin (0.009)	16	15	0.11	8-May-04	6	4	0.01	0.03	22-May-04

^[a] Laboratory reporting levels (LRLs) are shown in parentheses after the compound name, with degradate compounds in italics.

^[b] All units are in micrograms per liter (µg/L).

^[c] AMPA--aminomethylphosphonic acid; ESA--ethanesulfonic acid; OXA--oxanilic acid; SAA--sufinylacetic acid.

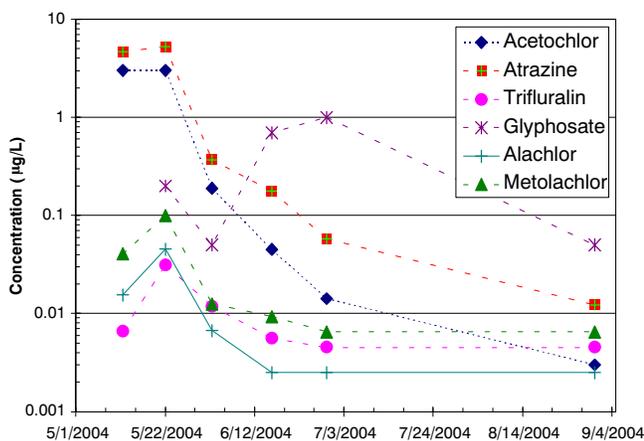


Figure 4. Acetochlor, atrazine, trifluralin, glyphosate, alachlor, and metolachlor concentrations in base flow samples. Non-detects for these herbicides are shown on the graph with a value equal to one half the laboratory reporting level (LRL; equal to 0.006, 0.007, 0.009, 0.1, 0.005, and 0.013 µg/L for acetochlor, atrazine, trifluralin, glyphosate, alachlor, and metolachlor, respectively).

concentration in 2004 base flow samples for the alachlor and metolachlor degradates also occurred in May, except for metolachlor ESA, which occurred on 31 August. Overall, detected alachlor and its degradates, and metolachlor and metolachlor OXA showed a decreasing concentration trend through the summer, whereas metolachlor ESA did not show a particular trend. The trends suggest that the source of alachlor and at least of portion of the metolachlor detections may have been from rain, while the lack of trends in metolachlor ESA may also suggest desorption from soil particles of metolachlor parent deposited in rains earlier in the year or metolachlor applications outside the watershed at times later in the growing season which were transported by

rain into this watershed. The rain and lysimeter (see location on fig. 1) sample concentrations are generally larger than base flow concentrations in the stream (fig. 5A and 5B), combined with the maximum storm-event stream sample metolachlor concentration occurring in July (table 2) would further support rainfall as a potential source of these compounds.

During the months of July and August, irrigation of part of the watershed from an on-site groundwater well also helped sustain base flow. Analysis of this groundwater, which originated from over 100 m depth, however, revealed no detectable levels of any of these herbicides or degradates. Analysis of water from a seep at the headwaters of the stream during August showed detectable concentrations of deethylatrazine (0.01 µg/L), alachlor ESA (0.16 µg/L), atrazine (0.01 µg/L), and trifluralin (0.01 µg/L). The larger concentrations of acetochlor, atrazine, and deethylatrazine in lysimeter samples than the stream base flow samples during July and August (fig. 5C, 5D, 5E), further supports the hypothesis of shallow subsurface transport to the stream as a potential source of these herbicides during base flow conditions. Trifluralin was not detected, and glyphosate and AMPA were not analyzed, in lysimeter samples. Further discussions of pesticide detections in water from the lysimeters at this site are included in Hancock et al. (2008).

The estimated annual load for 2004, percentage of maximum load during the week of maximum load, and LAPU (for parent compounds) of the herbicides analyzed for this study are shown in table 3. In any given year the week of maximum load will vary somewhat based upon rainfall, but with consistent rainfall, year-to-year herbicide application, and tillage practices the seasonal loading patterns would likely be generally the same. During the week of the first storm after application, approximately 84% and 73% of the

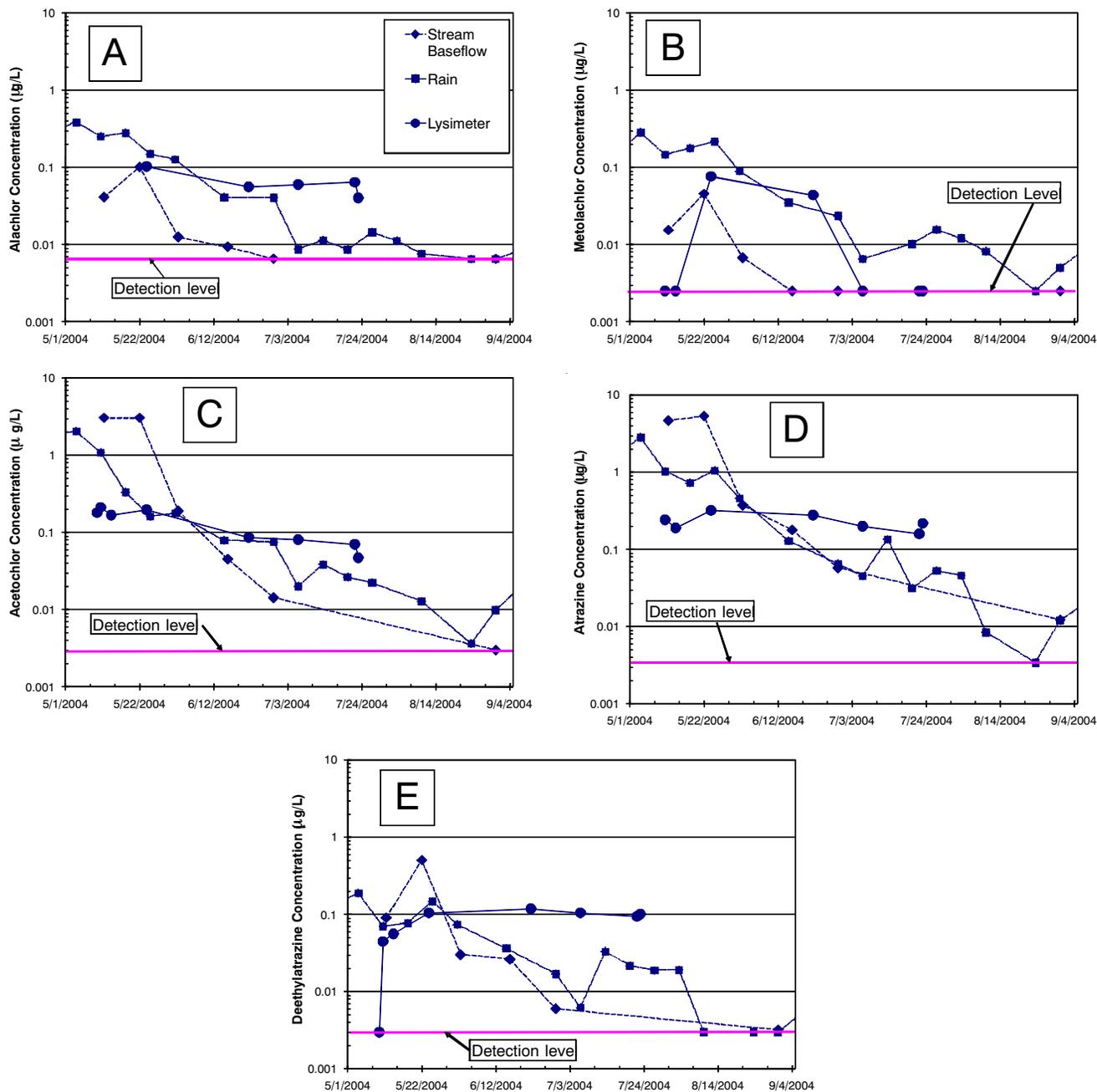


Figure 5. Herbicide concentrations of (A) alachlor, (B) metolachlor, (C) acetochlor, (D) atrazine, and (E) deethylatrazine in stream base flow, rain, and lysimeter samples collected during May through September 2004.

total annual loads of acetochlor and atrazine parent compounds, respectively, were transported out of the watershed via the stream. All degradate compounds for these two herbicides, except acetochlor/metolachlor ESA - 2nd amide, had their week of peak transported load about 3 weeks after application. Trifluralin also had its peak loading week about 3 weeks after application, but the magnitude of its total annual load was more than two magnitudes less than those for acetochlor and atrazine, despite comparable application rates. At this site trifluralin was incorporated into the soil, while acetochlor and atrazine were surface applied, and therefore trifluralin had less exposure to runoff. Additionally, trifluralin would be expected to be tightly bound to particles ($K_{oc} = 8,000 \text{ mL/g}$, table 1), and because only the dissolved fraction of trifluralin was analyzed on these filtered samples,

a large portion of the total trifluralin in the stream may have remained bound to particles that were filtered out before analysis. Glyphosate and its degradate, AMPA, also had their largest load during the week of the first storm after application, although the percent of annual load transported during that week was smaller than for acetochlor or atrazine. Glyphosate sorbs strongly to soil particles ($K_{oc} = 24,000 \text{ mL/g}$) relative to acetochlor and atrazine ($K_{oc} = 240$ and 100 mL/g , respectively), so additional glyphosate was likely transported out of the watershed sorbed onto suspended sediment in the stream, which was not analyzed in these filtered samples. This would be especially relevant during the first storm after application since glyphosate has a relatively short half life ($t_{1/2}$ in soil = 2 days) and would likely not persist in the soil for a long period of time. A lower

percentage of load during the week of the first storm could also be a result of a less well-defined period of application for glyphosate in the surrounding areas, which occurs from May through July. Alachlor and alachlor SAA peak loads occurred during the third week of May, while the transport of other alachlor degradates did not peak until July. The annual load of alachlor in the stream, which was not applied within this watershed but was used in the surrounding area (Fredrick et al., 2006), was approximately 2.5 orders of magnitude less than the annual loads for acetochlor and atrazine. The week of peak load of the other alachlor degradates (ESA, OXA, and ESA-2nd amide) and metolachlor and its degradates occurred during July.

Atrazine had the highest LAPU, followed by acetochlor, glyphosate, and trifluralin (table 3) of the herbicides applied within the watershed. The LAPU values for atrazine and trifluralin were within one standard deviation of the mean reported by Capel et al. (2001) for these herbicides on watersheds between 100 and 100,000 ha. Capel et al. (2001) did not calculate LAPU values for acetochlor or glyphosate. For alachlor and metolachlor, which were not applied by farmers in the study watershed in 2004, the LAPU values were greater than the ranges reported by Capel et al. (2001) for watersheds between 100 and 100,000 ha where the herbicides were applied by farmers in the watershed (mean \pm SD: $0.38 \pm 0.83\%$ and $1.0 \pm 1.6\%$, respectively). This may be because the herbicides deposited in the rain are introduced at nearly the same time they are removed through runoff to the stream, while herbicide that is applied by the farmer may stay in the soil for days or weeks after application. Biodegradation of the compounds by microbes attached to soil particles would likely not occur between the time of introduction to the field and removal by the stream when the herbicides are deposited in rain. As a result, the LAPU will be greater for the herbicides introduced to the soil by rain and immediately removed by runoff than for herbicides applied to the soil days or weeks before a storm.

Samples were collected as flow-weighted composites, along with grab samples, when possible, during the rise, peak, and fall of stream hydrographs during storm events when possible. Rainfall and streamflow were sampled during a 13.7-mm storm on 10 May 2004 (composite, rise, peak, and fall samples collected), a 60.2-mm storm on 22 May 2004 (composite and peak sample collected), and a 12.9-mm storm on 7 July 2004 (composite, first peak, and second peak samples collected). The storm on 7 July was a relatively small bimodal hydrograph, during which one flow-weighted composite sample plus a grab sample at each peak were collected. For each storm, herbicides and their degradates had variable peak times and concentrations (table 4).

During the 10 May storm, approximately one week after planting and concurrent application of acetochlor, atrazine, and trifluralin, the peak concentrations of acetochlor, atrazine, and their degradates were detected during the falling limb of the hydrograph. Comparison of stream concentrations during the storm to those in the rain and base flow (collected 12 May) indicated that most of the transported herbicide mass was a result of transport induced by the storm. However, the highest detected concentrations were during the falling limb, also suggesting that the herbicides derived from a longer-flowpath or slower-moving process than solely surface runoff, such as shallow subsurface transport. Similarly, the highest concentrations occurred

Table 3. Estimated annual load, percent of annual load during the week of largest load, and load as a percentage of use in the unnamed tributary to the South Fork of Dry Creek during 2004.

Herbicide or Degradate ^[a]	Estimated Annual Loading (g)	% Load in Week of Largest Load	Week of Largest Load	LAPU ^[b] (%)
Glyphosate	28	41	7-13 July	0.13
<i>AMPA</i>	38	33	7-13 July	na
Acetochlor	250	84	8-14 May	0.89
<i>Acetochlor ESA</i>	70	24	21-27 May	na
<i>Acetochlor OXA</i>	120	38	21-27 May	na
<i>Acetochlor SAA</i>	53	43	21-27 May	na
<i>Acetochlor/Metolachlor ESA-2nd amide</i>	11	15	8-14 July	na
Alachlor	0.75	30	21-27 May	1.20 ^[a]
<i>Alachlor ESA</i>	3.2	32	7-13 July	na
<i>Alachlor OXA</i>	1.3	23	7-13 July	na
<i>Alachlor SAA</i>	11	47	21-27 May	na
<i>Alachlor ESA-2nd amide</i>	0.17	74	3-9 July	na
Metolachlor	3.3	38	7-13 July	3.83 ^[c]
<i>Metolachlor ESA</i>	4.4	16	3-9 July	na
<i>Metolachlor OXA</i>	2.5	15	5-11 July	na
Atrazine	270	73	8-14 May	2.34
<i>Deethyl-atrazine</i>	11	34	22-28 May	na
Trifluralin	0.93	17	21-27 May	0.002

^[a] Degradate compounds are in italics. AMPA -- aminomethylphosphonic acid; ESA -- ethanesulfonic acid; OXA -- oxanilic acid; SAA -- sufinylacetic acid.

^[b] LAPU -- load as a percentage of use.

^[c] Since there was no reported application within the watershed for alachlor and metolachlor, use was estimated by pesticide deposition in rainfall from Vogel et al. (2008).

during the falling limb of the hydrograph in a tile-drained watershed, as a result of the herbicides moving through the shallow subsurface soil to the tiles and then being discharged to the stream (Kronvang et al., 2003). This hypothesis was tested by comparing the concentrations of chloride and sulfate at different points in the hydrograph, in rainfall, and in base flow samples. Base flow concentrations of these conservative ions would be representative of shallow sub-surface matrix flow, which reflects the chemistry of water that has had more contact time with soils (Steenhuis et al., 1994). Although direct overland flow samples were not collected to allow for a mixing analysis, the chloride and sulfate concentrations in stream water would be a qualitative estimate of the relative contributions of water from surface runoff and shallow subsurface flow to stream flow, i.e., the higher the concentration, the greater the contribution there would be from subsurface flow. The maximum concentrations of chloride and sulfate were detected on the rising limb (table 4), indicative of relatively less surface runoff influence during those parts of the storm hydrograph.

Comparison of base flow before the storm on 22 May to base flow on 12 May indicates that for acetochlor and atrazine and their degradates, the base flow concentrations increased or stayed about the same during this time period. For the other two storms shown in table 4, shorter storm duration did not allow for the collection of rise, peak, and fall samples with the autosamplers. For the storm on 22 May, a composite sample and a sample collected at approximately

Table 4. Concentrations of selected herbicides and degradate compounds, chloride, and sulfate in composite and grab samples collected during selected storms in 2004 from the unnamed tributary of the South Fork of Dry Creek and in rainfall samples collected in the watershed.

Herbicide ^[a]	12 May ^[b]		10 May				22 May		May 22		29 June		July 7		
	Baseflow (12:20)	Composite (01:00-05:46)	Rain ^[c]	Rise (01:48)	Peak (02:44)	Fall (04:46)	Baseflow (10:20)	Composite (18:31-20:39)	Rain (19:30)	Peak (19:30)	Baseflow (10:10)	Composite (14:47-18:33)	Peak One Rain (15:00)	Peak Two (16:35)	
Glyphosate	na	0.2	na	0.2	0.3	0.3	0.2	0.1	na	0.1	1.0	4.5	na	1.0	9.7
AMPA	na	0.8	na	0.8	1.0	1.0	0.7	0.5	na	0.4	1.2	5.4	na	1.4	5.2
Acetochlor	3.03	49	2.03	11.5	49.2	73.3	3.03	5.40	0.162	3.35	0.01	0.70	0.02	1.84	0.08
<i>Acetochlor ESA</i>	0.49	5.07	<0.02	1.27	4.04	7.04	5.38	4.3	<0.02	2.15	0.12	0.79	<0.02	0.81	0.39
<i>Acetochlor OXA</i>	0.69	10.0	<0.02	1.99	9.16	15.4	13.0	12.0	<0.02	5.97	0.05	0.89	<0.02	1.13	0.44
<i>Acetochlor SAA</i>	0.09	5.92	<0.02	0.78	5.36	8.47	5.44	6.33	<0.02	1.91	<0.02	0.17	<0.02	0.28	<0.02
<i>Acetochlor/ Metolachlor ESA - 2nd amide</i>	0.03	0.15	<0.02	0.07	0.16	0.25	0.53	0.17	<0.02	0.17	0.04	0.09	<0.02	0.10	<0.02
<i>Alachlor</i>	0.02	0.13	0.28	0.13	0.16	0.11	0.05	0.06	0.22	0.07	<0.005	<0.005	0.007	<0.005	<0.005
<i>Alachlor ESA</i>	0.09	0.08	<0.02	<0.02	0.03	0.12	0.03	0.03	<0.02	<0.02	<0.02	0.10	<0.02	0.06	0.03
<i>Alachlor OXA</i>	0.03	0.06	<0.02	0.02	0.05	0.10	0.05	0.05	<0.02	0.02	<0.02	0.04	<0.02	0.03	0.04
<i>Alachlor SAA</i>	0.06	1.14	<0.02	0.29	1.13	2.01	1.29	1.43	<0.02	0.74	<0.02	<0.02	<0.02	<0.02	<0.02
<i>Alachlor ESA - 2nd amide</i>	<0.02	<0.02	<0.02	<0.02	0.14	0.09	<0.02	<0.02	<0.02	<0.02	<0.02	0.03	<0.02	0.02	0.03
<i>Metolachlor</i>	0.04	0.31	0.38	0.37	0.32	0.25	0.10	0.15	0.15	0.26	<0.013	0.27	0.009	0.73	<0.035
<i>Metolachlor ESA</i>	0.14	0.07	<0.02	0.19	0.08	0.10	0.15	0.09	<0.02	0.15	0.05	0.14	<0.02	0.16	<0.02
<i>Metolachlor OXA</i>	0.03	0.05	<0.02	0.12	0.05	0.05	0.06	0.08	<0.02	0.17	0.02	0.06	<0.02	0.10	<0.02
Atrazine	4.65	58.4	2.83	15.6	58.6	85.6	5.27	9.16	1.05	4.64	0.06	1.11	0.05	0.18	0.06
<i>Deethylatrazine</i>	0.09	1.44	0.19	0.44	1.64	1.67	0.51	1.04	0.15	0.69	0.006	0.19	0.01	0.41	0.07
Trifluralin	0.007	0.044	0.021	0.011	0.052	0.038	0.031	0.042	0.025	0.017	<0.009	0.004	0.003	0.004	0.004
Chloride(mg/L)	11.3	4.1	<1.0	5.1	3.9	4.4	8.5	2.7	<1.0	2.2	13	8.8	<1.0	5.4	11
Sulfate (mg/L)	56.8	14	<1.0	23	12	15	51	10	<1.0	9.8	62	36	<1.0	22	49

^[a] Herbicides in italics are degradate compounds of the herbicide above it that is not italicized; AMPA: aminomethylphosphonic acid; ESA: ethane sulfonic acid; OXA:oxanilic acid; SAA: sulfynil acetic acid; 2nd: second; mg/L: milligrams per liter.

^[b] Number in parentheses under sample type is sample collection time

^[c] Rain is a weekly composite sample; All concentrations in micrograms per liter unless noted.

the storm peak (corresponding to the point of maximum concentration in many surface-water runoff studies) were collected. Comparison of composite sample concentrations to concentrations in the sample collected at approximately the peak of this storm indicated that this point on the hydrograph did not represent the point of maximum concentration for atrazine, acetochlor, and their degradates, consistent with the results of 10 May when the peak concentrations were during the falling limb of the hydrograph. Relative to the base flow concentrations on this date, the surface runoff also appears to dilute the concentration of acetochlor degradates in the stream. However, acetochlor, atrazine, and deethylatrazine appeared to have distinguishable contributions from surface runoff during the 22 May storm. During the storm on 7 July, the largest concentrations of acetochlor, atrazine, and their degradates were detected at the first peak of the bimodal storm, and concentrations in rainfall were minimal. The first peak also occurred at the approximate lag time of the surface-water runoff and at the time when chloride and sulfate concentrations indicate there was the largest influence of surface water. All of these suggest that these herbicides in the stream during this storm derived from a “first flush” in surface runoff.

Trifluralin was applied within the watershed concurrently with acetochlor and atrazine. However, concentrations of trifluralin in stream water were lower than for either acetochlor or atrazine (tables 2 and 4) because of the incorporation of trifluralin into the soil and greater K_{oc} values. The maximum detected concentrations of dissolved trifluralin, chloride, and sulfate during the 10 May storm was at the peak of the hydrograph, indicating that the dominant contribution of trifluralin in the filtered samples was from surface runoff; trifluralin associated with particles was not included in this analysis. The median K_{oc} value for trifluralin has been reported to be 8,000 mL/g (table 1), so it is expected that the compound would be sorbed to sediment particles and that these analyses would underrepresent the total mass of trifluralin transport in the stream during the 10 May storm. During the 7 July storm, trifluralin concentrations in the stream had fallen to below the laboratory reporting level, and suggests high volatilization rate (vapor pressure = 0.0147 Pa, Henry’s Law constant = 16.4 Pa·m³/mole; from Capel et al., 2008) and high sorption rates (K_{oc} = 8,000 mL/g; table 1) could partly account for the low concentrations.

Within the study watershed, glyphosate was applied one time during the study period on 5 July. Before this time, glyphosate and AMPA concentrations during storms and in

base flow samples were all relatively low -- $\leq 1.0 \mu\text{g/L}$ (table 4). During the bimodal storm on 7 July (two days after application), the highest concentration occurred at the second peak of the storm. The occurrence of the glyphosate and AMPA peak concentrations at this point of the storm suggests shallow subsurface transport of these herbicides, but requires further study to determine its exact mode of transport. The sorption of glyphosate has been shown to increase strongly with increasing contents of iron and aluminum (Piccolo et al., 1994; Gerritse et al., 1996; Day et al., 1997). Organic carbon content and pH have varying effects on sorption of glyphosate to soil (Carlisle and Trevors, 1988; Roy et al., 1989; Gerritse et al., 1996; Morillo et al., 2000; Gimsing et al., 2004). Additionally, phosphate may at times complement or compete with glyphosate for sorption sites (Dion et al., 2001; Gimsing et al., 2004). Glyphosate also coordinates strongly with heavy metals (Glass, 1984; Subramanian and Hoggard, 1988; McBride, 1991; Morillo et al., 2000). The chemical properties for glyphosate are somewhat contradictory, as it tightly binds to soil ($K_{oc} = 24,000 \text{ mL/g}$; table 1), but is also highly soluble [solubility= $10,100 \text{ mg/L}$; this is two to three magnitudes larger than the solubility of acetochlor and atrazine (Capel et al., 2008)].

Although alachlor and metolachlor were not reported to have been applied within the watershed in 2004, both the parent compound and some degradates of these herbicides were detected in the stream water. Alachlor and metolachlor were observed in rainfall, but their degradates were not. The source of these compounds at that time was likely from deposition of the parent in rainfall and subsequent degradation by soil microbes to form the degradates, because these herbicides had reportedly not been applied within the watershed. Alachlor and metolachlor degradates exhibited

the same seasonal concentration patterns as atrazine and acetochlor. The relatively large increase in stream base flow concentration of alachlor SAA between the 12 and 22 May base flow samples is also notable since the only reported source of alachlor during that time was from rainfall. Concentrations of metolachlor and its degradates during the 7 July storm had maxima during the first peak of the bimodal storm hydrograph, indicating that these compounds likely originated from surface runoff.

SUMMARY AND CONCLUSIONS

Herbicide transport has been investigated for six parent and 12 degradate compounds in an intermediate size watershed in eastern Nebraska. A summary of the timing of maximum load in the stream, along with the type of transport at that time is shown in table 5. In this intermediate-size watershed the timing of maximum load and primary mode of transport varied for the different herbicides. Generally, the herbicides that were applied within the watershed had maximum load during the week of the first storm after application, with shallow subsurface flow as the primary mode of transport. The exception was trifluralin, which had peak loading in the stream 3 weeks after application because of its soil incorporation rather than surface application. However, trifluralin would be expected to be strongly sorbed to soil particles, so the majority of this herbicide may have been transported out of the watershed sorbed to particles in the stream during this or a different storm, instead of being in the dissolved phase. For this reason, the trifluralin that was detected in the dissolved phase appeared to be transported with the surface runoff; however, that may not have been the situation for most of the total mass of trifluralin that was

Table 5. Summary of the timing of maximum load in the stream and the primary mode of transport during the time of maximum load, for six parent and 12 degradate herbicide compounds for the unnamed tributary to the South Fork of Dry Creek in eastern Nebraska during the growing season, 2004.

Herbicide or Degradate ^[a]	Timing of Maximum Load	Primary Mode of Transport at Time of Maximum Load
Glyphosate (applied within watershed)	Week of first storm after application within watershed	Shallow subsurface flow during storm
<i>AMPA</i>	Week of first storm after application within watershed	Shallow subsurface flow during storm
Acetochlor (applied within watershed)	Week of first storm after application	Shallow subsurface flow during storm
<i>Acetochlor ESA</i>	Three weeks after application	Shallow subsurface flow during storm
<i>Acetochlor OXA</i>	Three weeks after application	Shallow subsurface flow during storm
<i>Acetochlor SAA</i>	Three weeks after application	Shallow subsurface flow during storm
<i>Acetochlor/Metolachlor ESA- 2nd amide</i>	Two months after application	Surface runoff
Alachlor (not applied within watershed)	Two-three weeks after application in the region	Shallow subsurface flow during storm
<i>Alachlor ESA</i>	Two months after application in the region	Surface runoff
<i>Alachlor OXA</i>	Two months after application in the region	Surface runoff
<i>Alachlor SAA</i>	Two-three weeks after application in the region	Shallow subsurface flow during storm
<i>Alachlor ESA-2nd amide</i>	Two months after application in the region	Surface runoff
Metolachlor (not applied within watershed)	Two months after application in the region	Surface runoff
<i>Metolachlor ESA</i>	Two months after application in the region	Surface runoff
<i>Metolachlor OXA</i>	Two months after application in the region	Surface runoff
Atrazine (applied within watershed)	Week of first storm after application	Shallow subsurface flow during storm
<i>Deethyl-atrazine</i>	Three weeks after application in the area	Shallow subsurface flow during storm
Trifluralin (applied within watershed)	Three weeks after application in the area	Surface runoff

^[a] Degradate compounds are in italics; AMPA--aminomethylphosphonic acid; ESA--ethanesulfonic acid; OXA--oxanilic acid; SAA--sufinylacetic acid.

transported in the stream. Alachlor and metolachlor were not directly applied within the watershed, but did have detections within the stream. Alachlor and alachlor SAA had maximum loads 2 to 3 weeks after the general application period in the region and were primarily associated with shallow subsurface transport at that time, while the other alachlor degradates had maximum loads approximately 2 months after application in the area and were primarily associated with dissolved transport in surface runoff at that time. Metolachlor and its degradates also peaked a couple of months after primary application in the region and were primarily associated with dissolved transport in surface runoff.

The differences in the primary mode of transport for glyphosate, acetochlor, and atrazine at various times after application may be explained by differences in the method of application and physical properties of the compound. Many herbicides are applied as particles along with surfactants and other inert compounds. Perhaps during the first few weeks after application, the compounds remain in this particle phase and are gradually dissolved during the first few storms, while at later times after application the herbicides that remain in the environment are sorbed to the surface of soil particles. Further research is needed on this question.

The LAPU was calculated for the six parent compounds analyzed in the study, four of which had been previously reported by Capel et al. (2001). Atrazine and acetochlor, which were applied within the watershed, has similar LAPU values to those reported by Capel et al. (2001), but alachlor and metolachlor, which were apparently only deposited by rain within the watershed or may have had carry-over from previous rainfall deposition, had larger LAPU values than those reported by Capel et al. (2001). The LAPU may be larger in this instance because when herbicides were deposited by the concurrent rainfall, there would be less time for the compound to be degraded by microbes in the soil before reaching the stream than when applied by the farmer.

ACKNOWLEDGEMENTS

This research was supported by the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program. The authors would like to express their thanks for the interpretative guidance provided by Paul Capel (USGS), Joseph Domagalski (USGS), and Ronald Zelt (USGS). Numerous USGS colleagues assisted with installation, sample collection, and data management, and their involvement in the successful completion of the project was invaluable. Finally, we would like to thank the landowners in the watershed for their cooperation during this project.

REFERENCES

Anderson, C. W., T. M. Wood, and J. L. Morace. 1997. Distribution of dissolved pesticides and other water quality constituents in small streams, and their relation to land use, in the Willamette River Basin, Oregon, 1996. USGS Water-Resources Investigations Report 97-4268. Portland, Oreg.: U.S. Geological Survey.

Barbash, J. E. 2003. The geochemistry of pesticides. In *Treatise on Geochemistry*, 541-577. H. D. Holland and K. K. Turekian, eds. Oxford: Pergamon.

Bartlett, P. A., and Koepke, B. E. 1975. *Soil survey of Dodge County, Nebraska*. Washington D.C.: USDA, Soil Conservation Service, and University of Nebraska.

Bureau of Reclamation. 2001. Chapter 7: Weirs. In *Water measurement manual-A guide to effective water measurement practices for better water management*. Denver, Colo.: U.S. Department of the Interior, Bureau of Reclamation, Water Resources Research Laboratory. Available at http://www.usbr.gov/pmts/hydraulics_lab/pubs/wmm/. Accessed 9 February 2006.

Capel, P. D., and S. J. Larson. 2001. Effect of scale on the behavior of atrazine in surface waters. *Environ. Sci. Technol.* 35(4): 648-657.

Capel, P. D., S. J. Larson, and T. A. Winterstein. 2001. The behaviour of 39 pesticides in surface waters as a function of scale. *Hydrol. Process.* 15(7): 1251-1269.

Capel, P. D., K. A. McCarthy, and J. E. Barbash. 2008. National, holistic, watershed-scale approach to understand the sources, transport, and fate of agricultural chemicals. *J. Environ. Qual.* 37(3): 983-993.

Carlisle, S. M., and J. T. Trevors. 1988. Glyphosate in the environment. *Water, Air Soil Pollut.* 39(3): 409-420.

Day, G. M., B. T. Hart, I. D. McKelvie, R. Beckett. 1997. Influence of natural organic matter on the sorption of biocides onto goethite. II. Glyphosate. *Environ. Technol.* 18(8): 781-794.

Dion, H. M., J. B. Harsh, and H. H. Hill, Jr. 2001. Competitive sorption between glyphosate and inorganic phosphate on clay minerals and low organic matter soils. *J. Radioanalytical and Nuclear Chemistry* 249(2): 385-390.

Dugan, J. T., and R. B. Zelt. 2000. Simulation and analysis of soil-water conditions in the Great Plains and adjacent areas, Central United States, 1951-80. USGS Water-Supply Paper 2427. Lincoln, Nebr.: U.S. Geological Survey.

Fredrick, B. S., J. I. Linard, and J. L. Carpenter. 2006. Environmental Setting of Maple Creek Watershed, Nebraska. USGS Scientific Investigations Report 2006-5037. Lincoln, Nebr.: U.S. Geological Survey.

Fulford, J. M. 1998. User's Guide to the U.S. Geological Survey Culvert Analysis Program, Version 97-08. USGS Water-Resources Investigations Report 98-4166. Stennis Space Center, Miss.: U.S. Geological Survey.

Gassman, P. W., M. R. Reyes, C. H. Green, J. G. Arnold. 2007. The Soil and Water Assessment Tool: Historical development, applications, and future research directions. *Trans. ASABE* 50(4): 1211-1250.

Gerritse, R. G., J. Beltrán, and F. Hernández. 1996. Adsorption of atrazine, simazine, and glyphosate in soils of the Gngara Mound, Western Australia. *Aust. J. Soil Res.* 34(4):599-607.

Gimsing, A. L., O. K. Borggaard, and M. Bang. 2004. Influence of soil composition on adsorption of glyphosate and phosphate by contrasting Danish surface soils. *Eur. J. Soil Sci.* 55(1): 183-191.

Glass, R.L. 1984. Metal complex formation by glyphosate. *J. Agric. Food Chem.* 32(6): 1249-1253.

Hancock, T. C., M. W. Sandstrom, J. R. Vogel, R. M. T. Webb, E. R. Bayless, and J. E. Barbash. 2008. Pesticide fate and transport throughout unsaturated zones in five agricultural settings, USA. *J. Environ. Qual.* 37(3): 1086-1100.

Howard, P. H., ed. 1989. Pesticides. In *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*, 8-22. Chelsea, Mich.: Lewis Publishers.

Huntzinger, T. L., and M. J. Ellis. 1993. Central Nebraska river basins, Nebraska. *Water Resour. Bull.* 29(4): 533-574.

Hyer, K. E., G. M. Hornberger, and J. S. Herman. 2001. Processes controlling the episodic streamwater transport of atrazine and other agrochemicals in an agricultural watershed. *J. Hydrol.* 254(1-4): 47-66.

Kiely, T., D. Davidson, and A. Grube. 2004. Pesticides Industry Sales and Usage--2000 and 2001 Market Estimates. Washington, D.C.: United States Environmental Protection Agency.

- Kilpatrick, F. A., and J. F. Wilson, Jr. 1989. Measurement of time of travel in streams by dye tracing. (rev.). Techniques of Water-Resources Investigations of USGS, TWRI 03-A9. Washington D.C.: U.S. Geological Survey.
- Kronvang, B., H. L. Iversen, K. Vejrup, B. B. Mogensen, A.-M. Hansen, and L. B. Hansen. 2003. Pesticides in streams and subsurface drainage water within two arable catchments in Denmark: Pesticide application, concentration, transport and fate. Pesticides Research No. 69. Copenhagen, Denmark: Danish Environmental Protection Agency.
- Lee, E. A., and A. P. Strahan. 2003. Methods of Analysis of the U.S. Geological Survey Organic Geochemistry Research Group--Determination of Acetamide Herbicides and Their Degradation Products In Water Using Online Solid-Phase Extraction and Liquid Chromatography/Mass Spectrometry. USGS Open-File Report 03-173. Lawrence, Kans.: U.S. Geological Survey.
- Lee, E. A., A. P. Strahan, and E. M. Thurman. 2002. Methods of Analysis by the U.S. Geological Survey Organic Geochemistry Research Group--Determination of Glyphosate, Aminomethylphosphonic Acid, and Glufosinate in Water Using Online Solid-Phase Extraction and High-Performance Liquid Chromatography/Mass Spectrometry. USGS Open-File Report 01-454. Lawrence, Kans.: U.S. Geological Survey.
- Leu, C., H. Singer, S. R. Muller, R. P. Schwarzenbach, and C. Stamm. 2005. Comparison of atrazine losses in three small headwater catchments. *J. Environ. Qual.* 34(5):1873-1882.
- McBride, M. B. 1991. Electron spin resonance study of copper ion complexation by glyphosate and related ligands. *Soil Sci. Soc. Am. J.* 55(4): 979-985.
- McHale, M. R., and P. J. Phillips. 2001. Stream-water Chemistry, Nutrients, and Pesticides in Town Brook, a Headwater Stream of the Cannonsville Reservoir Watershed, Delaware County, New York, 1999. USGS Water-Resources Investigations Report 01-4050. Troy, N.Y.: U.S. Geological Survey.
- Morillo, E., T. Undabeytia, C. Maqueda, and A. Ramos. 2000. Glyphosate adsorption on soils of different characteristics: Influence of copper addition. *Chemosphere* 40(1): 103-107.
- Neitsch, S. L., J. G. Arnold, J. R. Kinry, J. R. Williams, and K. W. King. 2002. Soil and Water Assessment Tool Theoretical Documentation: Version 2000. College Station, Tex.: Texas Water Resources Institute. Available at: www.brc.tamus.edu/swat/doc.html. Accessed 17 August 2005.
- Pfaff, J. D. 1993. Method 300.0: Determination of Inorganic Anions by Ion Chromatography. Cincinnati, Ohio: U.S. Environmental Protection Agency, Accessed 22 January, 2008. Available at www.epa.gov/waterscience/methods/method/files/300_0.pdf
- Piccolo, A., G. Celano, M. Arienzo, and A. Mirabella. 1994. Adsorption and desorption of glyphosate in some European soils. *J. Environ. Sci. Health Bull.* 29(6): 1105-1115.
- Roman-Mas, A., C. P. Weisskopf, and S. J. Klaine. 1995. Mechanistic evaluation of pesticide temporal patterns for a first-order stream. In *Collection of short papers on the Beaver Creek watershed study in West Tennessee, 1989-1994*, 45. W.H. Doyle, Jr., and E.G. Baker, compilers. USGS Open-File Report 95-156. Nashville, Tenn.: U.S. Geological Survey.
- Roy, D. N., S. K. Konar, S. Banerjee, D. A. Charles, D. G. Thompson, and R. Prasad. 1989. Persistence, movement and degradation of glyphosate in selected Canadian boreal forest soils. *J. Agric. Food Chem.* 37(2): 437-440.
- Schwarz, G. E., and R. B. Alexander. 1995. State soil geographic (STATSGO) data base for the conterminous United States. USGS Open-File Report 95-449. Reston, Va.: U.S. Geological Survey.
- Steenhuis, T. S., J. Boll, G. Shalit, J. S. Selker, and I. A. Merwin. 1994. A simple equation for predicting preferential flow solute concentrations. *J. Environ. Qual.* 23(5): 1058-1064.
- Subramanian, V., and P. E. Hoggard. 1988. Metal complexes of glyphosate. *J. Agric. Food Chem.* 36(6): 1326-1329.
- U.S. Department of Commerce. 2005. Annual climatological summary, 2004. Asheville, N. Car.: National Oceanic & Atmospheric Administration, National Climate Data Center. Available at cdo.ncdc.noaa.gov/ancsum/ACS. Accessed 06 October, 2005.
- U.S. Environmental Protection Agency (USEPA). 2004. BASINS: Better Assessment Science Integrating point & Nonpoint Sources. Washington, D.C.: United States Environmental Protection Agency. Available at www.epa.gov/waterscience/basins/index.html. Accessed August 2005.
- U.S. Geological Survey (USGS). 2006. The National Map Seamless Server. Reston, Va. U.S. Geological Survey. Available at seamless.usgs.gov. Accessed August 2005.
- Vogel, J. R., M. S. Majewski, and P. D. Capel. 2008. Pesticides in rain in four agricultural watersheds in the United States. *J. Environ. Qual.* 37(3): 1101-1115.
- Wauchope, R. D., T. M. Buttler, A. G. Hornsby, P. W. M. Augustijn-Beckers, and J. P. Burt. 1992. SCS/ARS/CES pesticide properties database for environmental decisionmaking. *Rev. Environ. Contam. Toxicol.* 123: 1-157.
- Williams, D. R., and M. E. Clark. 2001. Nutrients and Organic Compounds in Deer Creek and South Branch Plum Creek in Southwestern Pennsylvania, April 1996 through September 1998. USGS Water-Resources Investigations Report 00-4061. New Cumberland, Penn.: U.S. Geological Survey.
- Williams, R. J. 1998. Modelling pesticide runoff to surface waters. Part II--Model application. *Pestic. Sci.* 54(2): 121-130.
- Wu, T. L., D. L. Correll, and H. E. H. Remenapp. 1983. Herbicides runoff from experimental watersheds. *J. Environ. Qual.* 12(3): 330-336.
- Zaugg, S. D., M. W. Sandstrom, S. G. Smith, and K. M. Fehlberg. 1995. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of Pesticides in Water by C-18 Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry with Selected-Ion Monitoring. USGS Open-File Report 95-181. Denver, Colo.: U.S. Geological Survey.